U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-288 512

X-Ray Analysis of Airborne Asbestos Final Report: Design and Construction of a Prototype Asbestos Analyzer

(U.S.) Naval Research Lab, Washington, DC

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, NC

Aug 78

United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

EPA-600/2-78-194
August 1978

Research and Development

PB 288512

EPA

X-Ray Analysis of Airborne Asbestos

Final Report: Design and Construction of a Prototype Asbestos Analyzer

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-78-194		PB288512

4. TITLE AND SUBTITLE	5. REPORT DATE
X-RAY ANALYSIS OF AIRBORNE ASBESTOS Final Report: Design and Construction of a Prototype Asbestos Analyzer	August 1978 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	**8. PERFORMING ORGANIZATION REPORT NO.**
L. S. Birks, J. V. Gilfrich, and J. W. Sandelin	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	**10. PROGRAM ELEMENT NO.**
Radiation Technology Division Naval Research Laboratory Washington, D. C. 20375	1AD712 BA-25 (FY-77) **11. CONTRACT/GRANT NO.** EPA-IAG-D6-0651
12. SPONSORING AGENCY NAME AND ADDRESS	**13. TYPE OF REPORT AND PERIOD COVERED**
Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, N.C. 27711	Final 10/76-6/78 **14. SPONSORING AGENCY CODE** EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

A prototype asbestos analyzer has been designed and constructed for use by the Environmental Protection Agency. It incorporates the principle of broad-beam x-ray optics and the special fiber-aligned sample described in earlier reports (EPA-650/2-75-004 and EPA-600/2-77-062). The prototype instrument utilizes two detectors for simultaneous measurement of diffracted signal and background; the mass of asbestos is simply the net difference in intensity for these two detectors normalized by the sensitivity of the analyzer as determined using standards.

The prototype analyzer is contained in a vacuum box 15x15x32 cm and mounts on top of a standard commercial x-ray power supply. It uses a Cr target spectrographic tube which is located in a separate lead-shielded enclosure in the box. The mechanics of selecting the 2θ diffracting angles for different forms of asbestos are unique and especially designed to minimize the space required. The beam trap is a critical component of the instrument; it reduces the backscattered noise signal to less than 100 photons/sec from an incident beam of about 10^{11} photons/sec.

Preliminary tests with the analyzer indicate a sensitivity of 18 photons per second per μg of chrysotile and a calculated 3σ detection limit of 0.1 μg for a 500 second measurements. Amosite has a somewhat better sensitivity and detection limit.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution	Chrysotile	13B
* Asbestos	Amosite	08G
* Analyzers		11E
Design		14B
* X-ray diffraction		20F
* Alignment		07D
Quantitative analysis		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	27
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE A03 - A01

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-600/2-78-194
August 1978

X-RAY ANALYSIS OF AIRBORNE ASBESTOS

Final Report: Design and Construction of a Prototype Asbestos Analyzer

by

L. S. Birks, J. V. Gilfrich, and J. W. Sandelin

Radiation Technology Division
Naval Research Laboratory
Washington, D. C. 20375

Interagency Agreement EPA-IAG-D6-0651

Project Officer

Jack Wagman, Director

Emissions Measurement and Characterization Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N.C. 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A prototype asbestos analyzer has been designed and constructed for use by the Environmental Protection Agency. It incorporates the principle of broad-beam x-ray optics and the special fiber-aligned sample described in earlier reports under this interagency agreement (1,3). The prototype instrument utilizes two detectors for simultaneous measurement of diffracted signal and background; the mass of asbestos is simply the net difference in intensity for these two detectors normalized by the sensitivity of the analyzer as determined using standards.

The prototype analyzer is contained in a vacuum box 15x15x32 cm and mounts on top of a standard commercial x-ray power supply. It uses a Cr target spectrographic tube which is located in a separate lead-shielded enclosure in the box. The mechanics of selecting the 2θ diffracting angles for different forms of asbestos are unique and especially designed to minimize the space required. The beam trap is a critical component of the instrument; it reduces the backscattered noise signal to less than 100 photons/sec from an incident beam of about 10^{11} photons/sec.

Preliminary tests with the analyzer indicate a sensitivity of 18 photons per second per μg of chrysotile and a calculated 3σ detection limit of 0.1 μg for a 500 second measurement. Amosite has a somewhat better sensitivity and detection limit.

1. INTRODUCTION

In the first report under this interagency agreement (1), a new type of broad-beam x-ray optics was described, and a commercial x-ray spectrometer was modified to measure the diffracted intensity from aligned asbestos fibers in a special sample configuration. The 500 second, 3σ detection limit reported was 0.15 μg, nearly two orders of magnitude better than by any previously reported x-ray diffraction method (2). This favorable detectability coupled with the simplicity and projected low cost of the x-ray measurement compared to electron microscopy indicated considerable promise for large-scale routine analysis.

The second report of this series (3) described the specimen preparation technique and the problems encountered in aligning the asbestos fibers on the special grid used to produce an electrostatic field. Sonication to disperse the individual asbestos fibrils, ashing to remove organic matter, variation of the alignment medium, control of temperature and humidity were all described in Reference 3. This specimen-preparation effort to define the critical parameters has continued at the Environmental Sciences Research Laboratory of the Environmental Protection Agency (EPA), Research Triangle Park, N. C., resulting in a reproducible method of aligning the fibers, at least in the presence of a minimum of extraneous particulate material (personal communication, J. Wagman).

In this report we describe the design and construction of the working prototype asbestos analyzer instrument. It is based on the previous laboratory experiences and incorporates

a dual detector system for measuring signal and background simultaneously. Preliminary test results with the prototype instrument are given for samples containing known masses of standard asbestos. Further testing and analysis of real environmental samples (e.g., airborne, waterborne, quarried rock, iron ore, etc.) are planned by the EPA Environmental Sciences Research Laboratory.

2. SUMMARY

A prototype asbestos analyzer has been designed and constructed for EPA. It uses special x-ray optics and specimen preparation and can detect and identify as little as 0.1 μg of chrysotile or other asbestos fibers in a 500 second counting interval.

3. CONCLUSIONS

The asbestos analyzer allows fibrous asbestos to be distinguished uniquely from nonfibrous forms or clay minerals of similar crystallographic characteristics. It relies on sample preparation which causes the asbestos fibers to be oriented on a special grid, and on broad-beam x-ray optics which allows specific 2θ diffraction angles to be selected for large-area specimen deposits. It can detect submicrogram amounts of asbestos and measure them quantitatively. The capital investment in equipment and the time per analysis are both far less than for electron microscopy; thus the cost per analysis may be reduced by as much as a factor of ten. In terms of identification of specific asbestos forms and quantitation of the mass present the diffraction method appears better than electron microscopy on both counts. Thus the diffraction method may find its greatest application as a rapid, low-cost screening method for large scale analysis. If the total mass does not exceed prescribed limits, there is no need for expensive electron microscopy; if the mass is greater than the specified limits then electron microscopy of a similar sample might be appropriate.

4. RECOMMENDATIONS

The prototype asbestos analyzer should be calibrated for the various forms of asbestos using standard fibers prepared the same way as unknown samples. After calibration it should be tested by running a series of real specimens collected at selected asbestos emission sites. Comparison of at least some of the runs on real samples should be made by electron microscopy on aliquots collected from the same source and at the same time as the x-ray samples.

The x-ray method should be tested for interference by other particulate matter collected along with the asbestos. Generally this interference will be in the form of increased nondiffraction background but occasionally there may be partial overlap with the diffraction pattern of clay minerals or nonfibrous serpentines or amphiboles. Spiked samples containing known ratios of asbestos to bulk particulate matter can be prepared for the interference tests using standard asbestos. A recommended range of spiking would be from 1 part in 10 to 1 part in 1000.

5. REVIEW OF CONCEPTS

From the beginning of the work it has been recognized that ordinary x-ray diffraction procedures cannot distinguish chrysotile fibers from platy serpentine and likewise cannot distinguish other asbestos fibers from clay minerals with similar diffraction characteristics. Two factors had to be considered in order to provide a practicable method which could measure the net fiber content of samples containing interference from nonfibrous components. These two factors were:

1.) The fibers must be aligned parallel to each other in order to obtain preferred orientation in a diffraction pattern, Fig. 1.

2.) Photographic film cameras are not sensitive enough for the small mass of asbestos of interest, and the usual diffractometer optics are not suitable because crystal planes parallel to the fiber axis diffract equally well whatever the orientation of the specimen, Fig. 2.

To satisfy the two requirements a new sample preparation technique was necessary and a new type of x-ray optics had to be developed.

Sample Preparation. The scheme for aligning the asbestos fibers experienced many pitfalls as described in Reference 3. These difficulties have been overcome in the work carried out at the EPA laboratories, cited previously. In general the preparative method can be described in the following steps:

1.) A sample containing fibrous asbestos is filtered from air or water onto Millipore or similar substrate.

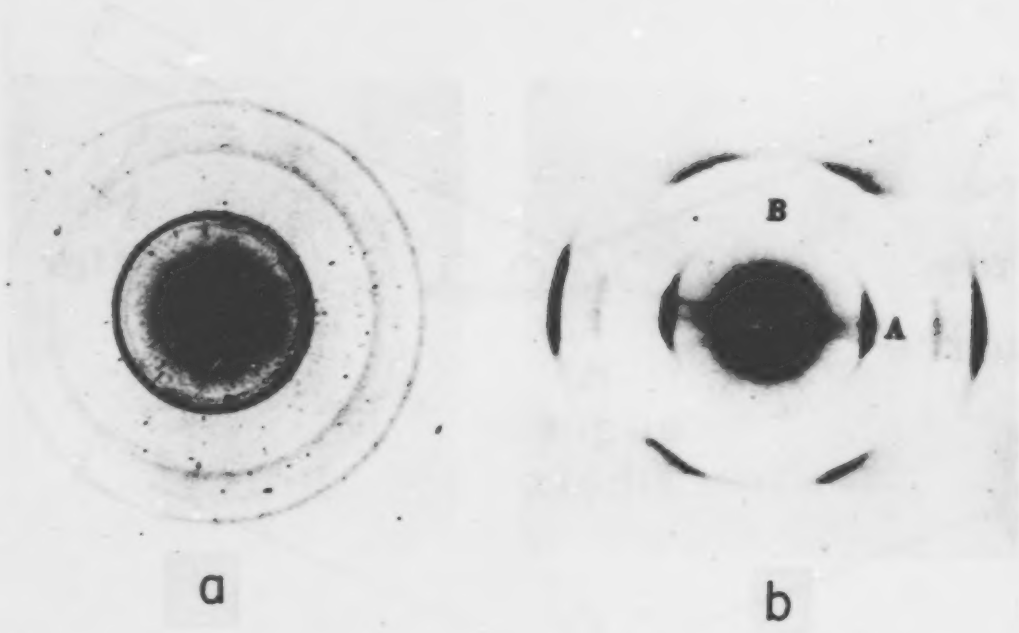

Fig. 1. X-ray powder diffraction patterns of chrysotile asbestos taken with photographic film: a.) unoriented fibers, b.) fibers oriented with axis vertical.

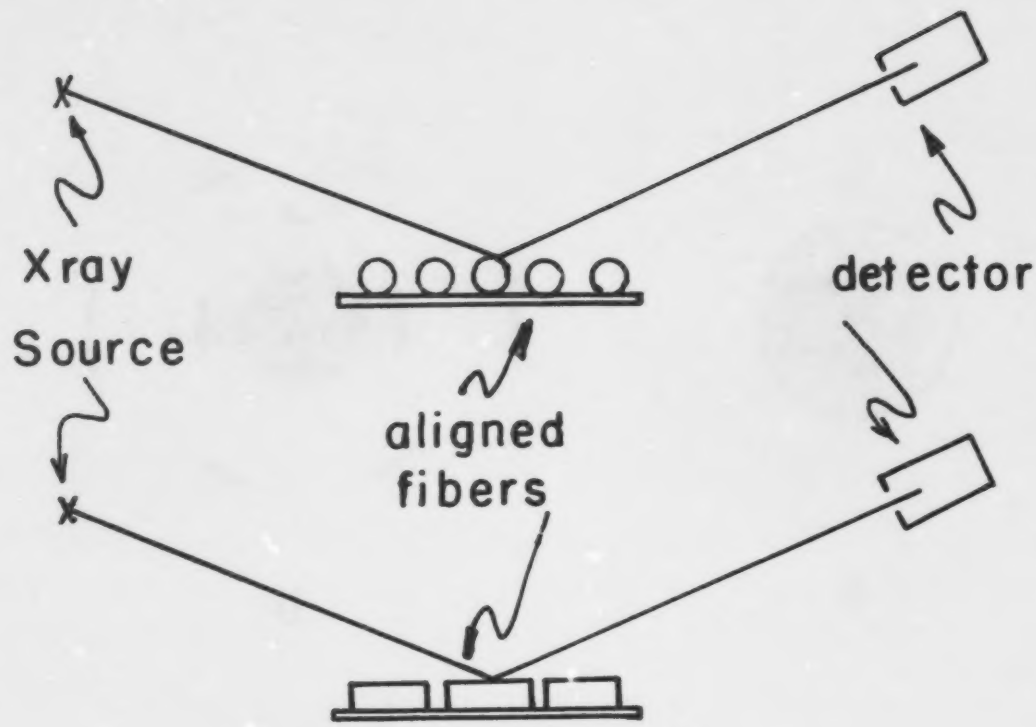

Fig. 2. Usual diffractometer optics allows diffraction from planes parallel to the fiber axis irrespective of the orientation of the fibers in the plane of the specimen.

2.) The substrate and other organic matter is removed by ashing. (Note, some technique for physically separating asbestos and the clay minerals from the bulk of other particulate material is desirable; work to this end is being sponsored by EPA.)

3.) The residue is suspended in 1 ml of water plus a wetting agent (1/2% aerosol OT) and sonicated vigorously to disperse the particles and break up the asbestos fibers into individual fibrils.

4.) The suspension is again filtered and ashed.

5.) This time the residue is taken up in the "alignment medium", (up to 0.1 ml of amyl acetate) and sonicated gently to disperse the particles.

6.) The amyl acetate is placed on a special alignment grid, Fig. 3, and a voltage applied to align the fibrous asbestos, Fig. 4.

7.) A thin film of nitrocellulose is sprayed on the grid, stripped off with the sample, and mounted on a support ring as the final specimen.

X-ray Optics. The parallel broad-beam optics developed is shown schematically in Fig. 5. Radiation from the large focal spot of a spectrographic x-ray tube is rendered parallel by the collimator and strikes the specimen which is mounted perpendicular to the beam. The strongest diffracting planes parallel to the fiber axis have large d-spacings (e.g. 002 planes in chrysotile: $d = 7.38$ Å). A Cr-target x-ray tube is chosen to provide the longest practical characteristic-line wavelength to diffract at as large a 2θ angle as possible. Background radiation at the same 2θ angle is contributed by scattering or diffraction from randomly oriented other particulate material and is of equal intensity at both detectors. Subtracting the intensity at Detector II from that at Detector I gives the net intensity from fibrous asbestos alone.

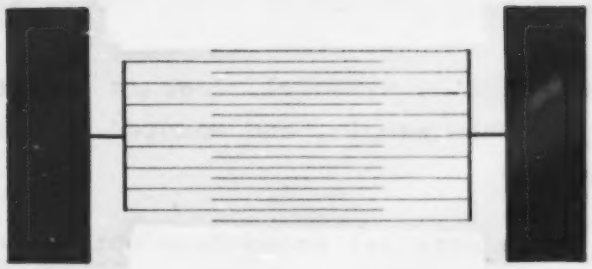

Fig. 3. Special multielectrode grid used in the alignment of asbestos fibers. Interelectrode distance is approximately 0.8 mm.

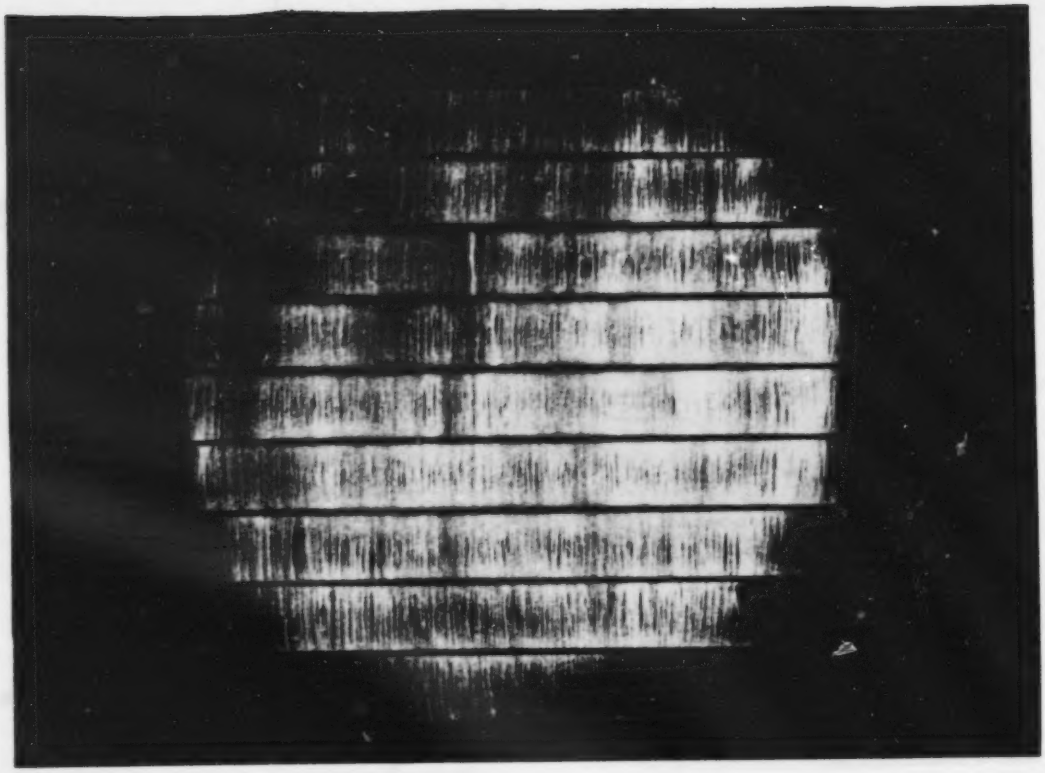

Fig. 4. Micrograph of asbestos fibers aligned across the special grid of Fig. 3.

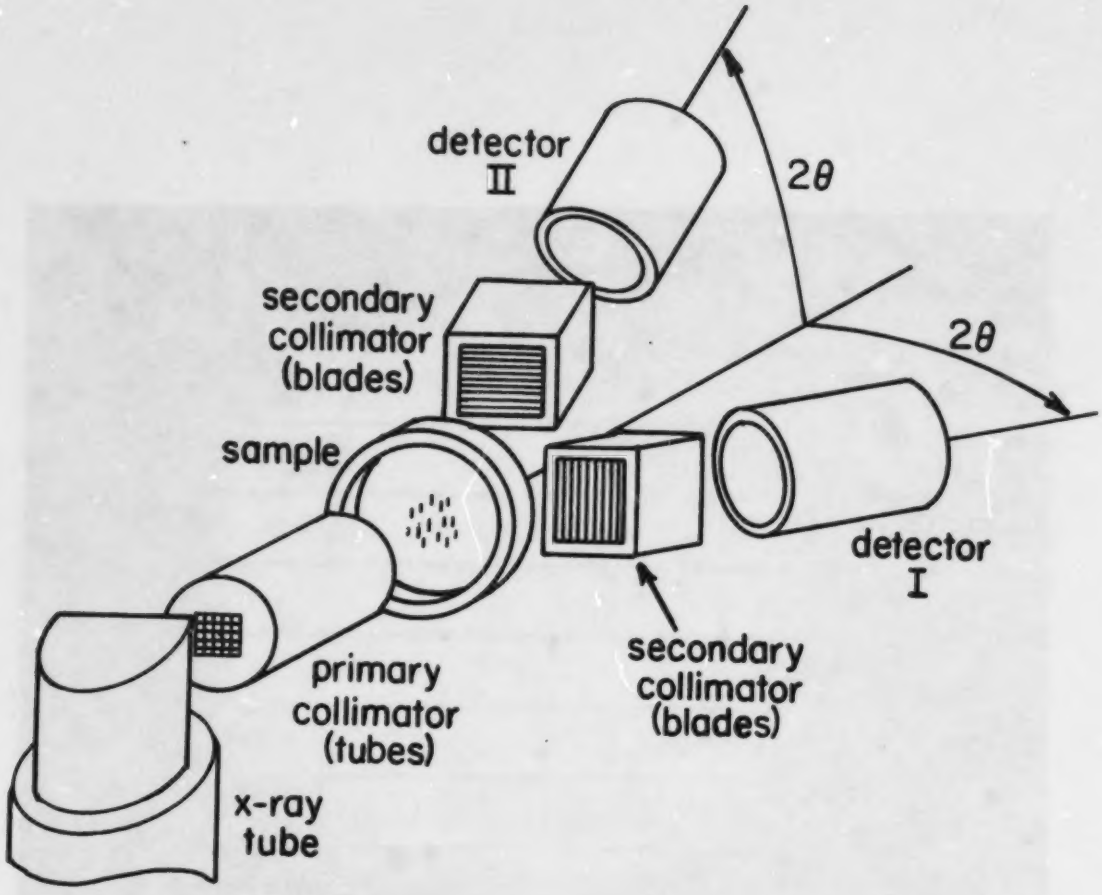

Fig. 5. Schematic of broad-beam x-ray optics for measurement of aligned asbestos fibers. Detector I measures the diffracted beam corresponding to the strong spot at position A in Fig. 1. Detector II measures the background corresponding to the position B in Fig. 1.

6. DESIGN OF THE ASBESTOS ANALYZER

Fig. 6 shows the layout of the vacuum box which contains the analyzer.

Primary Beam. The x-ray tube is in a lead-shielded compartment. The primary collimator extends from this compartment to the specimen; the collimator consists of a 10x10 array of square Ni tubes each 0.75 mm on a side and 50 mm long to allow passage of the beam from the 6x8 mm oval projected-size tube focal spot. The collimator housing extends almost to the specimen to prevent the detectors seeing scattering or fluorescence from the ends of the collimator tubes.

Sample Mount. The sample inserts on a stalk from the top of the box through a hole with an o-ring seal.

Vacuum. Pumping is with an ordinary mechanical pump and a vacuum of about 0.5 torr is achieved.

Setting the 2θ Angle. To simplify the mechanics of the secondary collimators they are mounted and driven as shown schematically in Fig. 7. The collimator is mounted on a segment of a large worm wheel with its axis offset from the specimen position. Thus radiation diffracted at different 2θ angles passes through different portions of the secondary collimator to the fixed detector as shown in Fig. 7.

Detectors. The two detectors are scintillation photomultipliers mounted outside the vacuum box. They view the diffracted radiation through vacuum-tight Be windows. Lead apertures inside the Be windows limit the angular range of the diffracted radiation between 14 and 20 degrees 2θ and thus insure that the

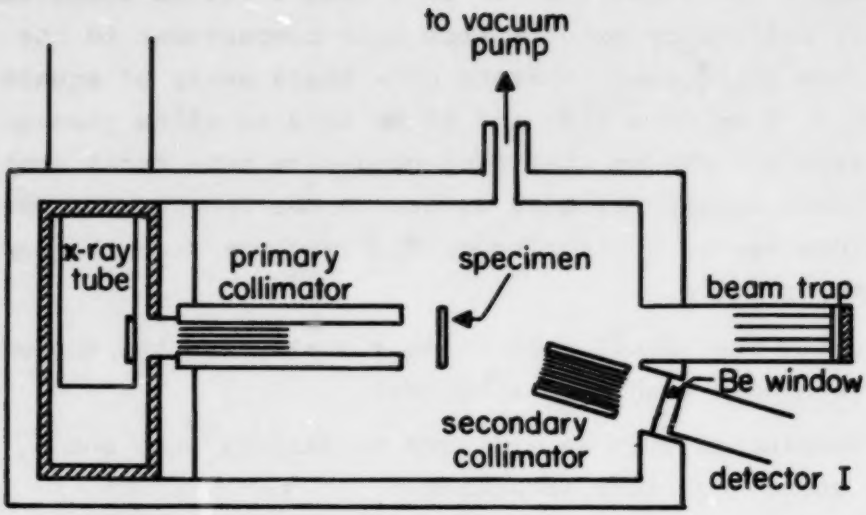

Fig. 6. Schematic of components. The detectors are outside the vacuum box (Detector II not shown so that the beam trap can be seen).

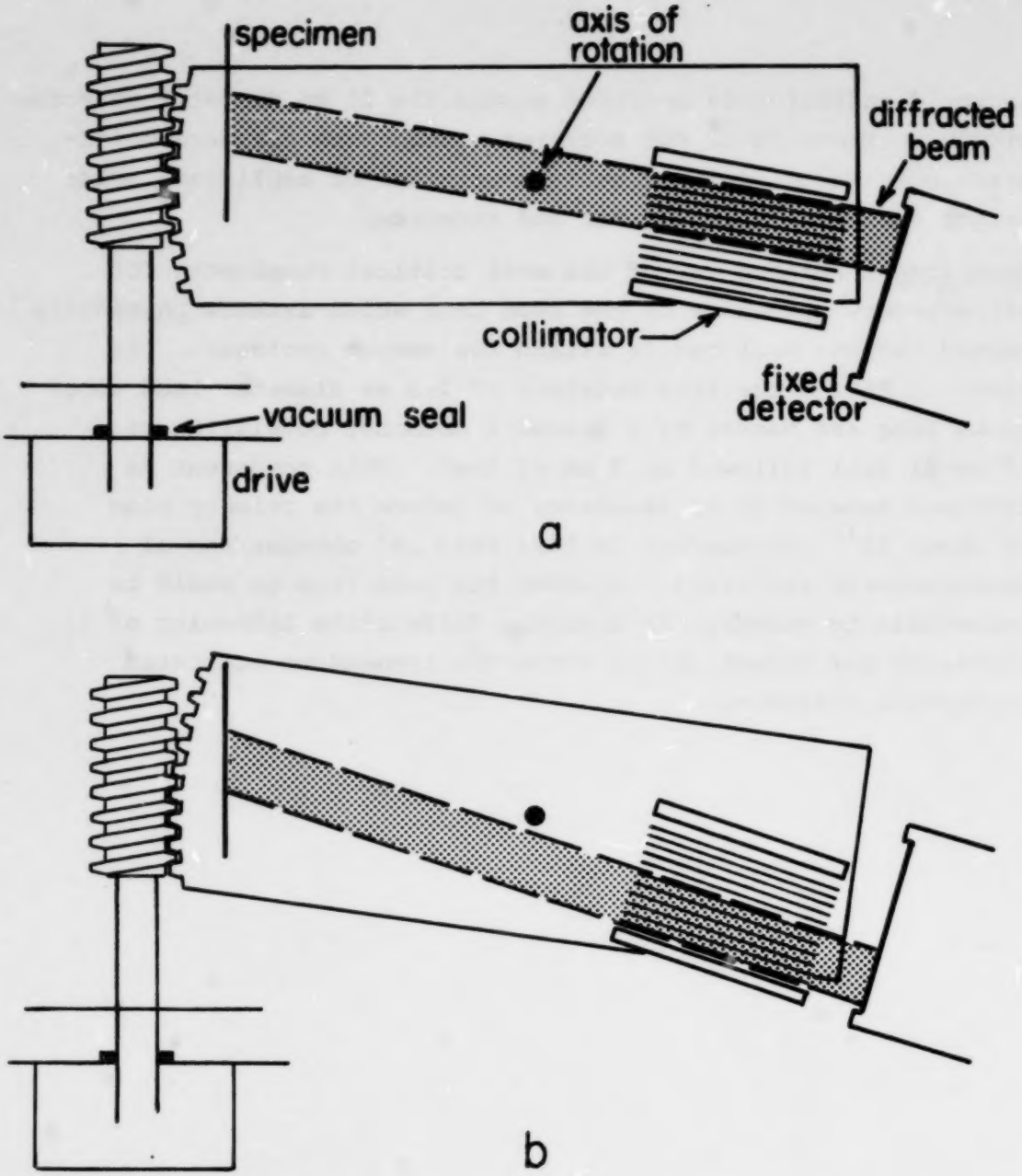

Fig. 7. Detail of drive mechanism for secondary collimator.
a.) With collimator set at minimum 2θ angle diffracted beam passes through inner portion of blades.
b.) With collimator set at maximum 2θ angle diffracted beam passes through outer portion of blades.

accepted radiation is confined within the 25 mm diameter detector windows. Electronics for detector readout are standard solid-state counting circuits usually consisting of amplifier, pulse height analyzer, scaler-timer and ratemeter.

Beam Trap. Perhaps one of the most critical components for satisfactory operation is the beam trap which extends physically beyond the box wall but is within the vacuum enclosure. As shown in Fig. 8 the trap consists of 2.5 mm diameter lead tubes 40 mm long and backed by a graded Z absorber consisting of 18 μm Al foil followed by 3 mm of lead. This component is critical because it is necessary to reduce the primary beam of about 10^{11} photons/sec to less than 10^{2} photons/sec of backscattered radiation. Without the beam trap it would be impossible to measure the asbestos diffraction intensity of 15-20 photons per second per μg above the tremendous scattered background intensity.

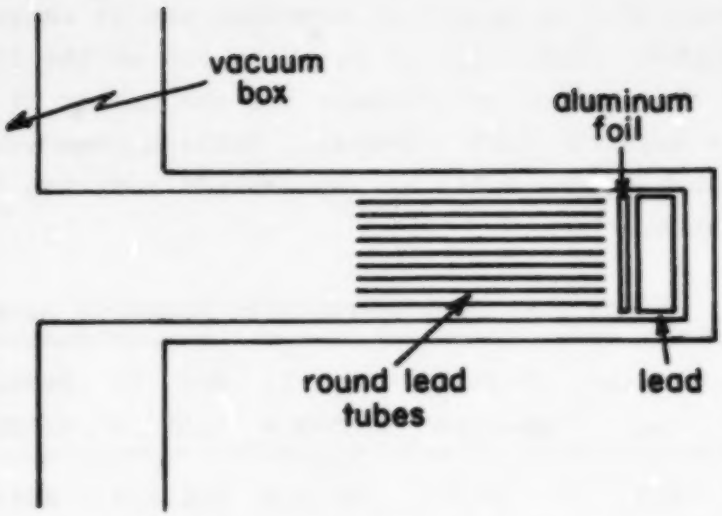

Fig. 8. Detail of beam trap. The lead tubes reduce the solid angle of backscatter. The aluminum foil reduces lead fluorescence from the lead backing.

7. PRELIMINARY TESTS OF THE ANALYZER

Aligned samples of standard chrysotile and amosite were used to test the operation of the instrument. Fig. 9 shows stripchart recordings of scans through the diffraction angle with each detector. In practice, scanning the 2θ range is not required. Rather, each detector would be set at the 2θ peak for the type of asbestos of interest and the number of photons counted for a selected time interval. Table 1 shows the results of 500 sec counting intervals at the peak 2θ position for each type of asbestos.

TABLE 1. X-RAY RESULTS FOR STANDARD ASBESTOS SAMPLES

Type	Quantity μg	2θ angle degrees	Det. I c/500 s	Det. II c/500 s	Sens,S c/500 s/μg	C_L μg
Chrysotile	5.3	17.8	148,212	100,818	8942	0.1
Amosite	∿5	15.9	233,788	175,195	11719	0.1

For an unknown sample the difference between Detector I and Detector II divided by the sensitivity, S, gives the mass of asbestos according to Eq. 1.

$$\text{mass in } \mu g = (\text{Detector I} - \text{Detector II})/S \qquad (1)$$

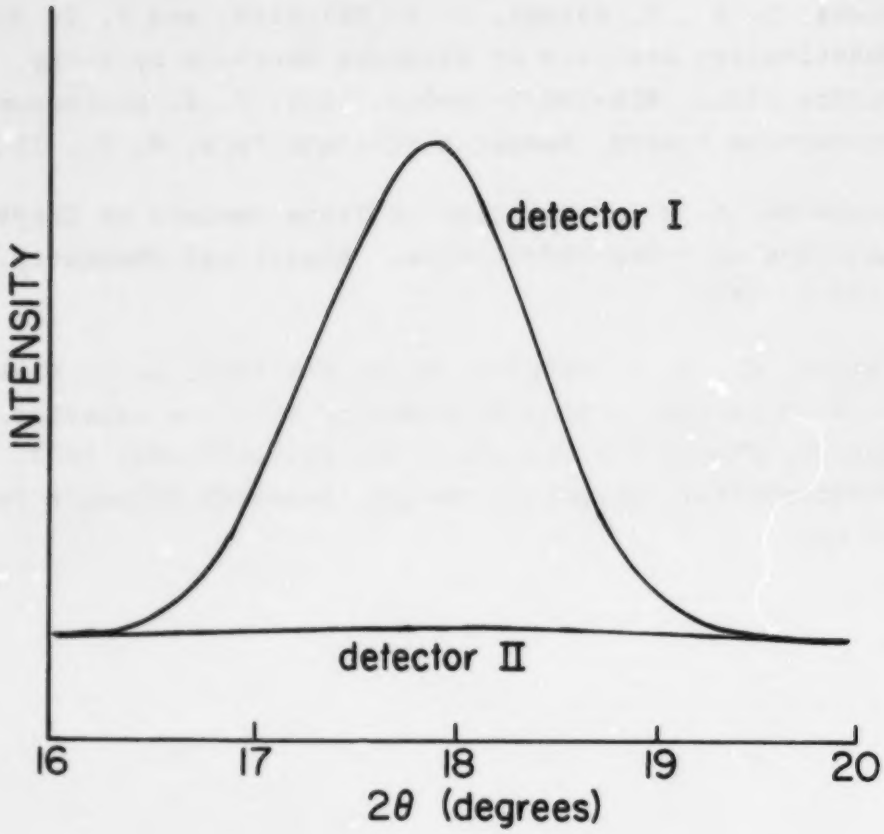

Fig. 9. Diffraction peak for chrysotile as recorded by Detector I and background as recorded by Detector II.

REFERENCES

1. Birks, L. S., M. Fatemi, J. V. Gilfrich, and E. T. Johnson. Quantitative Analysis of Airborne Asbestos by X-Ray Diffraction. EPA-650/2-75-004, 1975, U. S. Environmental Protection Agency, Research Triangle Park, N. C., 11 pp.

2. Rickards, A. L. Estimation of Trace Amounts of Chrysotile Asbestos by X-Ray Diffraction. Analytical Chemistry 44(11): 1872-3, 1972.

3. Fatemi, M., E. T. Johnson, R. R. Whitlock, L. S. Birks, and J. V. Gilfrich. X-Ray Analysis of Airborne Asbestos. Interim Report: Sample Preparation. EPA-600/2-77-062, 1977, U. S. Environmental Protection Agency, Research Triangle Park, N. C., 29 pp.